

Plutonium Speciation and Distribution in Soil Samples from the Rocky Flats Environmental Test Site

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Background:

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years. To properly control Pu migration in soils within Federal sites and onto public lands, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation and environmental transport is needed. The key scientific goals of the EMSP project we are conducting are: to determine Pu concentrations and speciation at a contaminated DOE site; to study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu species; to determine the mechanism(s) of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling; and to model the environmental behavior of plutonium. Our long-term goal is to use characterization, thermodynamics, mineral interactions, and mobility data to develop better models of radionuclide transport and risk assessment, and to enable the development of speciation-based decontamination strategies.

This research will fill important gaps between basic actinide science and the problems impeding site clean-up, plutonium disposition, and accurate risk assessment. Information gained will allow for the development of technologies and clean-up approaches targeting particular plutonium contaminants and improved assessment of risks associated with actinide migration, site remediation, and decontamination. By combining very specific study of plutonium at the Rocky Flats Environmental Test Site (RFETS), a well-characterized contaminated site, with laboratory studies on the most important plutonium and mineral component systems, we will provide essential knowledge of contaminant characteristics and distinguish critical geochemical processes and mechanisms. Herein we report summarize our results on characterizing samples from RFETS.

Technical Description of Work:

To determine Pu concentrations and speciation at RFETS we are using Thermal Ionization Mass Spectrometry (TIMS) to measure the isotopic $^{240}\text{Pu}/^{239}\text{Pu}$ ratio and identify the plutonium as originating from global fallout or site activities. For those water and soil samples having the highest concentrations we are using x-ray absorbance spectroscopy to determine the oxidation state and local coordination geometry (speciation) of the Pu. For particular samples we are performing physical separations and radionuclide counting to determine the characteristics of fractions containing portions of the Pu to determine overall concentrations; for example, size fractionation to determine the grain/soil size having the highest Pu concentration—macroscopic localization. We are

using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) to determine the morphology of components within samples, degree of microscopic localization, and association of Pu with other elements in soil samples. And we are using x-ray absorbance spectroscopy (XAS, EXAFS) to determine the oxidation state and coordination environment of Pu in environmental samples.

Samples from the RFETS which are most concentrated in Pu provide an opportunity to determine the speciation and other chemical and physical details of the contaminant Pu present. We have size fractionated soil samples from the 903 Pad area and analyzed each fraction using radionuclide decay counting, SEM, EDX, XAS, and decay radiography. SEM secondary electron images showed that the Pu in the soil fractions was delocalized down to at least the 100 Å scale. EDX analysis showed the samples were predominantly aluminosilicates and that Pu was not correlated with any other elements (Al, Si, K, and O dominated the spectra; other elements were absent or present in only some spots at trace levels). Particle track images are consistent with the SEM data; radiographs showed dispersed, omnidirectional tracks.

X-ray absorbance experiments were difficult because the 'standard' L_{III} spectra were not informative due to the presence of elements which absorb in the same energy range. Data were therefore obtained using the L_{II} absorption edge. Two of the fractions were sufficiently concentrated in plutonium to yield high quality spectral data. The near edge region of the spectrum has an absorbance maximum and edge indicative of Pu(IV). In fact, just after this measurement we measured the L_{II} absorbance of pure solid PuO_2 and found the two spectra had the same features (edge, maximum, no near-edge 'shoulder' indicative of Pu(V) or Pu(VI)) at the same energies. Analysis of the EXAFS data for the more concentrated of these two samples indicates there are approximately eight nearest neighbor atoms at a distance of 2.33 Å from the Pu in the soil sample, consistent with PuO_2 .

Not only is this the first definitive spectroscopic data on Pu in an environmental sample, but the data show the Pu in the most concentrated samples from the RFETS is in a highly stable and immobile form, the dioxide. The data also show that Pu is most concentrated in the 0.01-0.02 inch fractions, is dispersed on macroscopic and microscopic scales, and is not highly associated with any other particular element. These results should be very powerful and useful to RFETS personnel tasked with addressing concerns regarding plutonium migration from the site and for those tasked with remediating the site.

We attempted to determine the oxidation state and speciation of plutonium in several other samples, but in all other cases the concentration of Pu relative to other absorbing species was too low to obtain reliable, meaningful data. For example, a sample from a core from pond B-1 had a relatively high concentration of Zr or another element which has an absorption edge very close in energy to the Pu edge. (Zirconium has an absorption edge at 17999.35 eV; plutonium species have absorption edges of 18056, 18058, 18060 and 18061 eV for Pu III-VI, respectively). We did not observe an absorption edge corresponding to the Pu in this soil sample. We may attempt to measure the x-ray absorption of samples in this concentration range after a pre-concentration step.

Table 1. Fractionations of soils from the RFETS and Gross Gamma Counting Results.

	Size	Net CPS/g
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		gross gamma ²⁴¹ Am
A1	> .0234 inch	
A2*	0.0234-0.0164 inch	8.995
A3	0.0116-0.0164 inch	22.97
A4	>0.0116 inch	8.832
B1	> .0234 inch	
B2	0.0234-0.0164 inch	30.2
B3	0.0116-0.0164 inch	41.71
B4	>0.0116 inch	78.19



